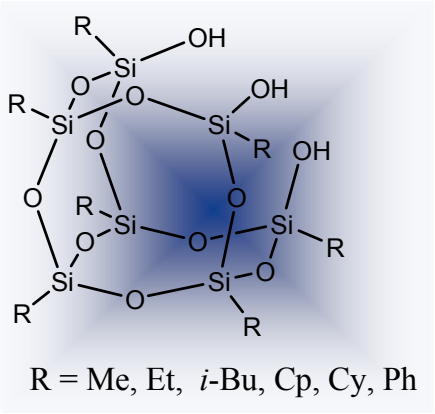
From Nanoscience to Nanotechnology: The Development and Application of Polyhedral Oligomeric Silsesquioxanes (POSS) as Versatile, Engineering Nanomaterials.



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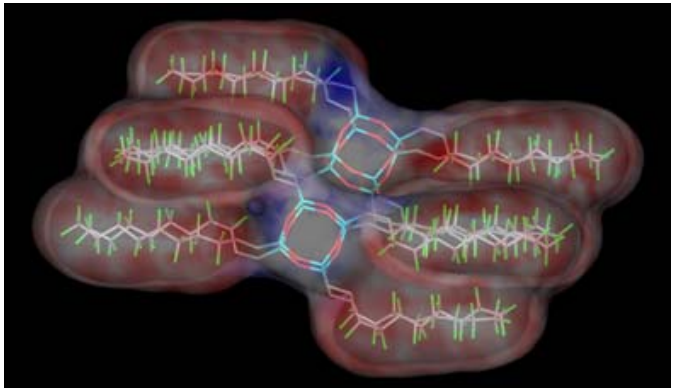

Dr. Shawn H. Phillips

Chief, Propulsion Materials Applications Branch

AFRL/PRSM

shawn.phillips@edwards.af.mil

Report Documentation Page

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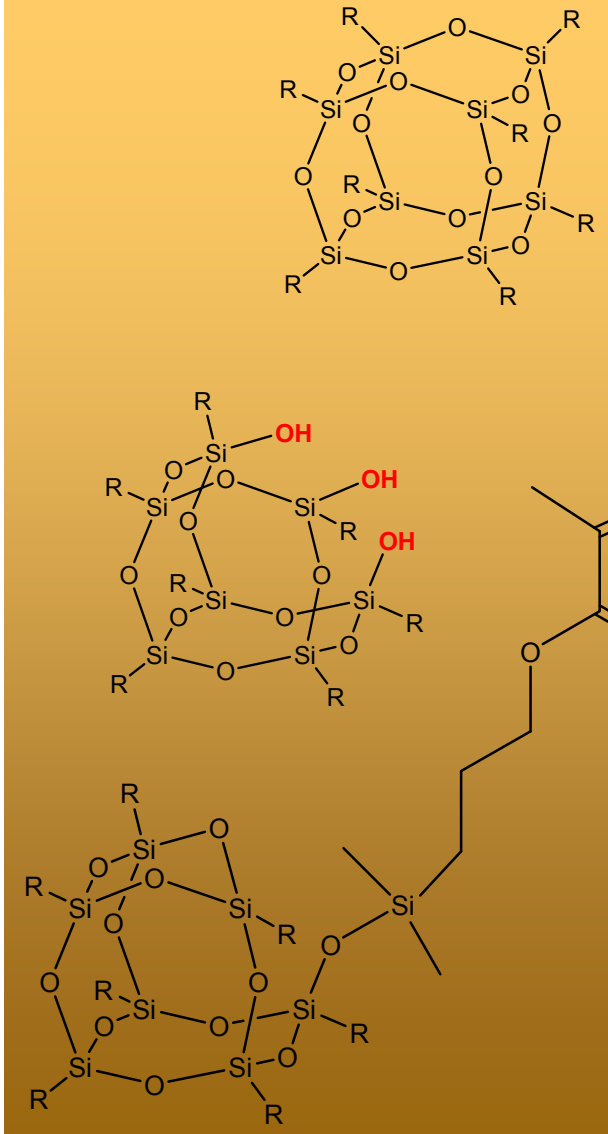
POSS: Where We Were (1996)

- **Cost: $5,000-$10,000/lb**
- **Volume: ~20 lbs/yr**
- **Production time: min 11 days, max 6 months**
- **Versatility: ~6 POSS feedstocks ~30 POSS macromers**
- **No successful POSS blends**
- **Made only by U.S. Government**



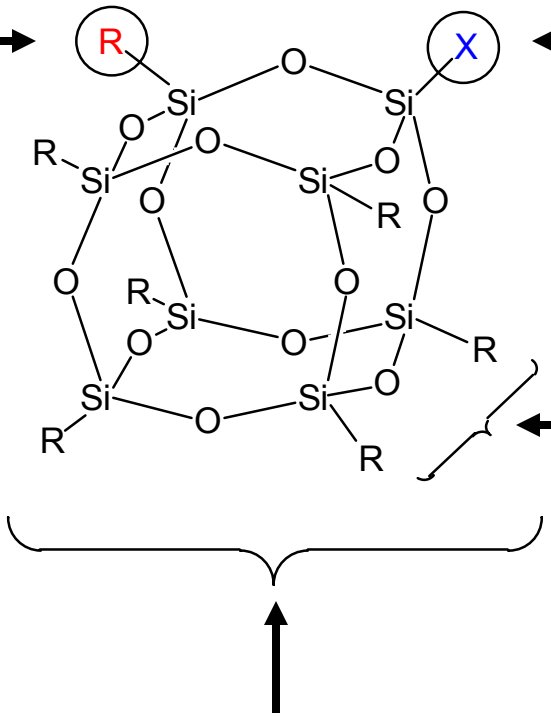
What Property Enhancements Can You Get From Using POSS?

- increased T_g
- increased T_{dec}
- enhanced blend miscibility
- reduced flammability
- extended temperature range
- oxidation resistance
- reduced heat evolution
- increased oxygen permeability
- altered mechanicals
- lower density
- lower thermal conductivity
- reduced viscosity
- disposal as silica
- thermoplastic or curable
- Beat competitors' patents !

Anatomy of a Polyhedral Oligomeric Silsesquioxane (POSS®) Molecule

Nonreactive organic (R) groups for solubilization and compatibilization.

May possess one or more functional groups suitable for polymerization or grafting.



Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

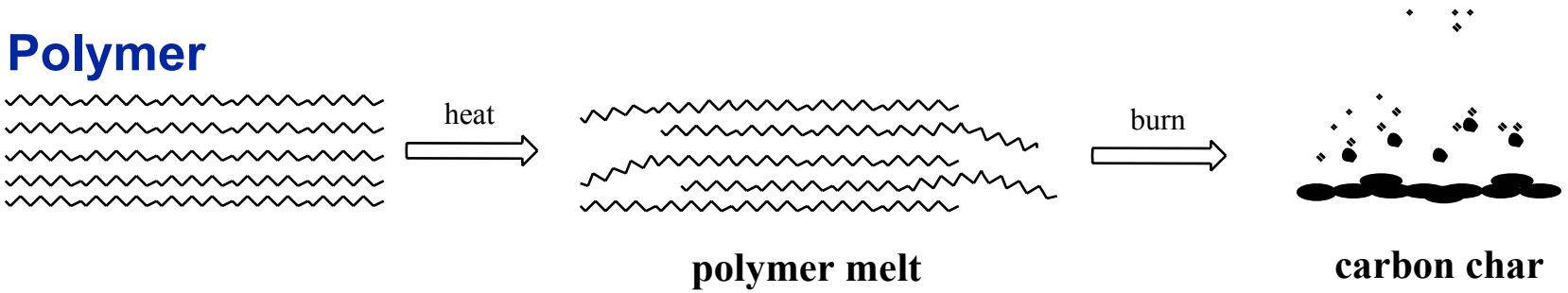
Thermally and chemically robust hybrid (organic-inorganic) framework.

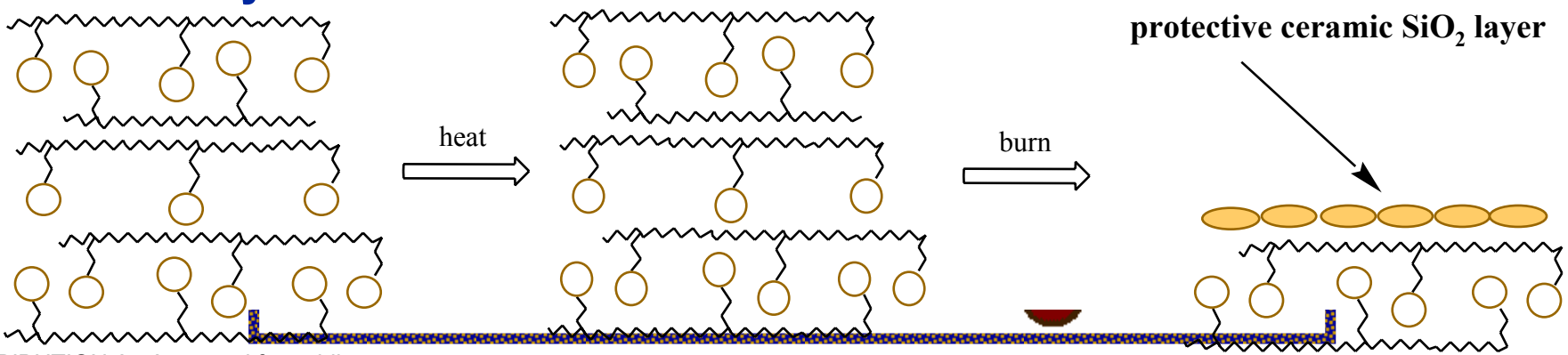
Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

- Think of it as functionalized sand, or smallest particle of sand possible

Oxidation Resistance/Reduced Flammability, Smoke & Heat Evolution

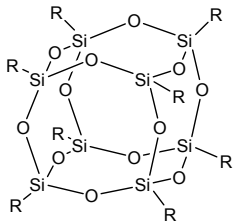
- Only organic groups on POSS cage can burn
- Silicon groups on POSS are only partially oxidized and form a ceramic silicon dioxide (SiO_2) layer in-situ
- POSS can form a char layer that stops the burning process





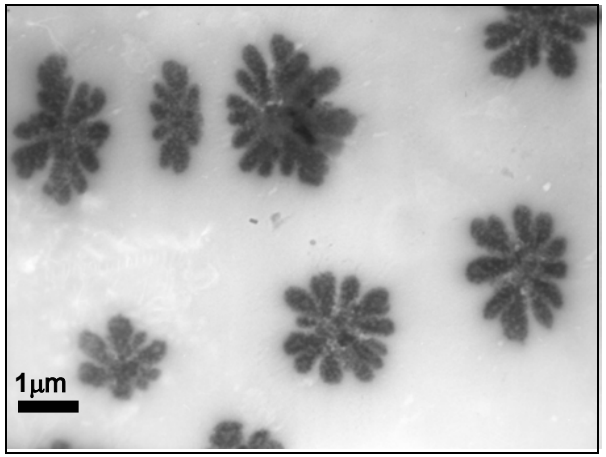
How to use POSS (Blends or Drop-In Nanofillers)

50 Wt % POSS Blends in 2 Million MW PS

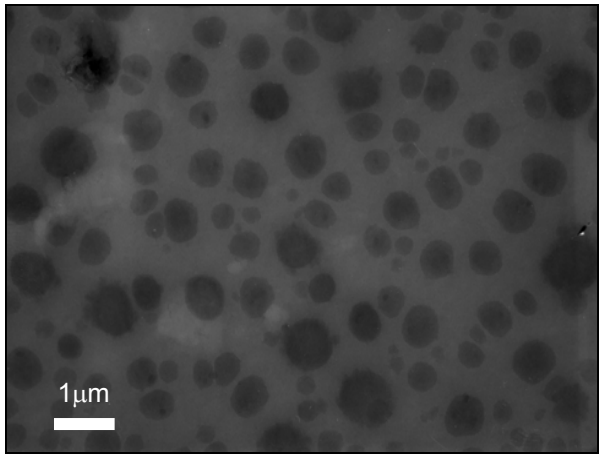


R = cyclopentyl

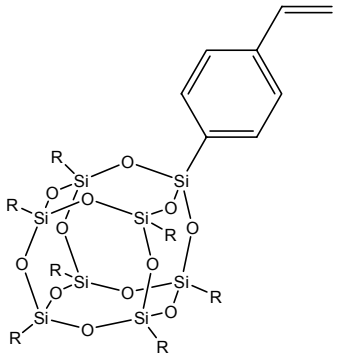
Cp_8T_8



Domain Formation

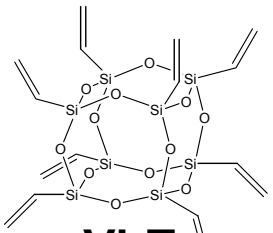


Partial Compatibility

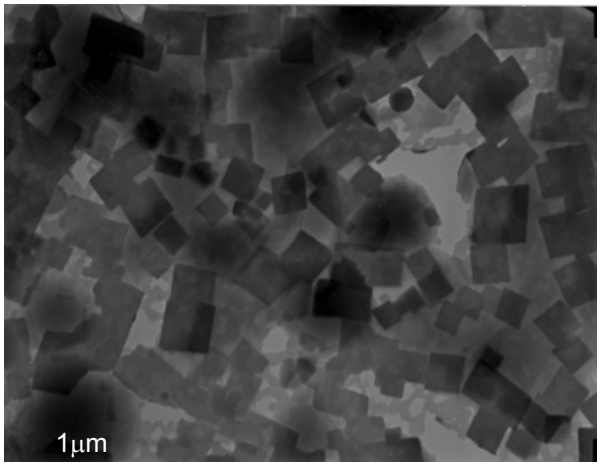


R = cyclopentyl

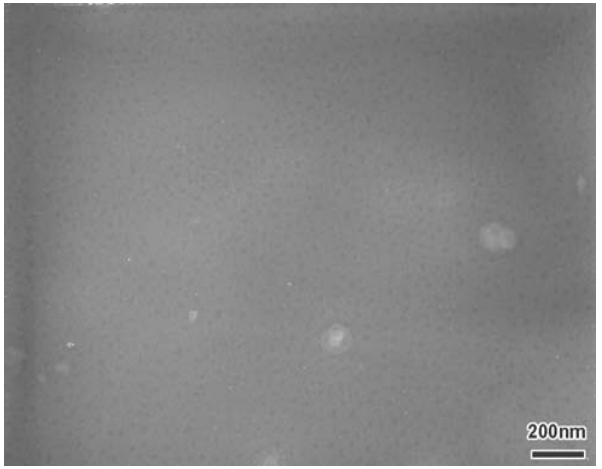
$Cp_7T_8Styryl$



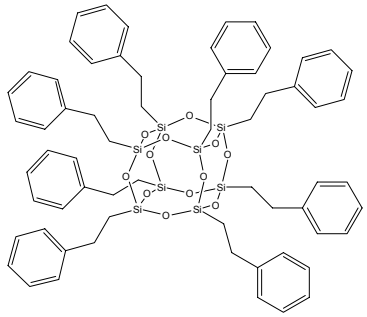
Vi_8T_8



Immiscible POSS Crystallites



Complete Compatibility-
POSS Nanodispersion/Transparent

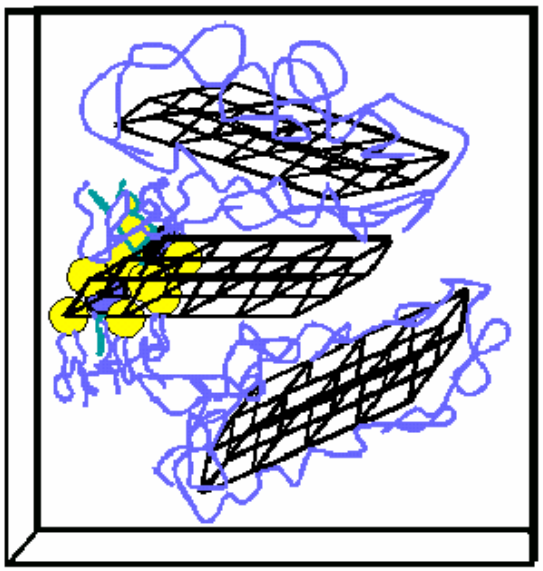


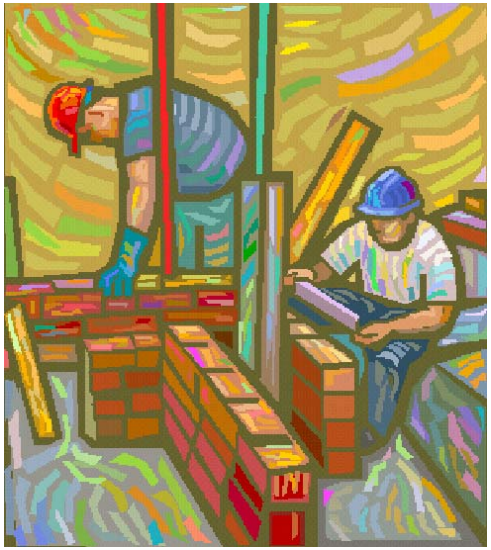
$Phenethyl_8T_8$

Blanski, et al., *Polymer Preprints*, **2000**. 41(1): p. 585.

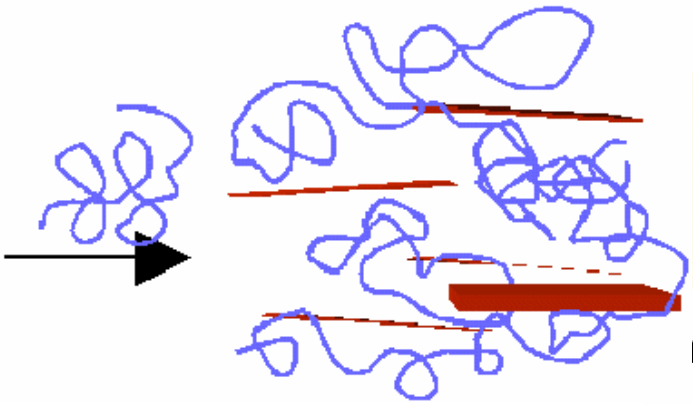
Coughlin Building Block Model (POSS Blends & Copolymers)

Bottom-up Approach
(Self-Assembly)



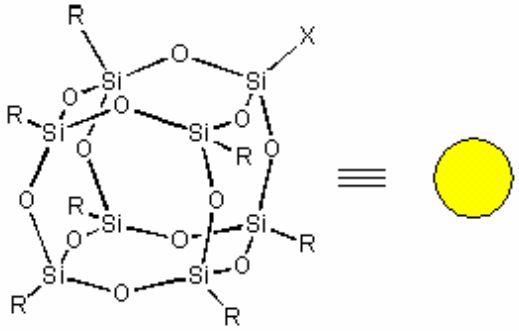


Top-down Approach

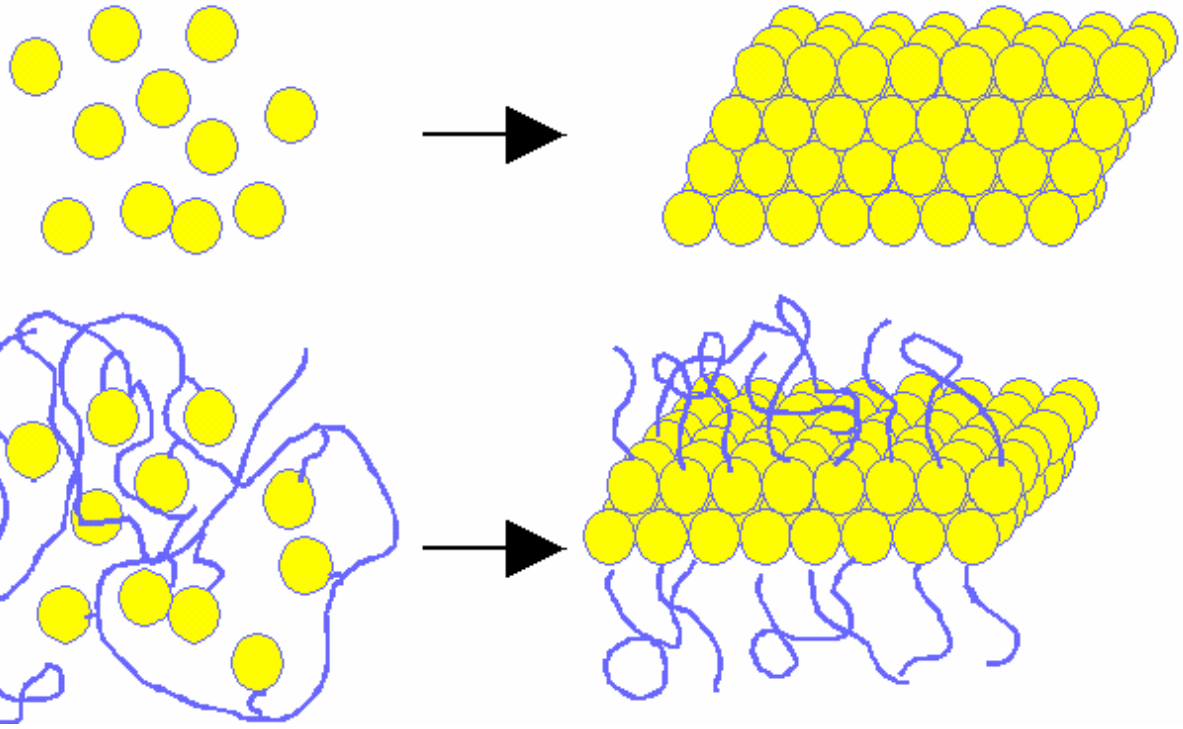


Bryan Coughlin-UMass

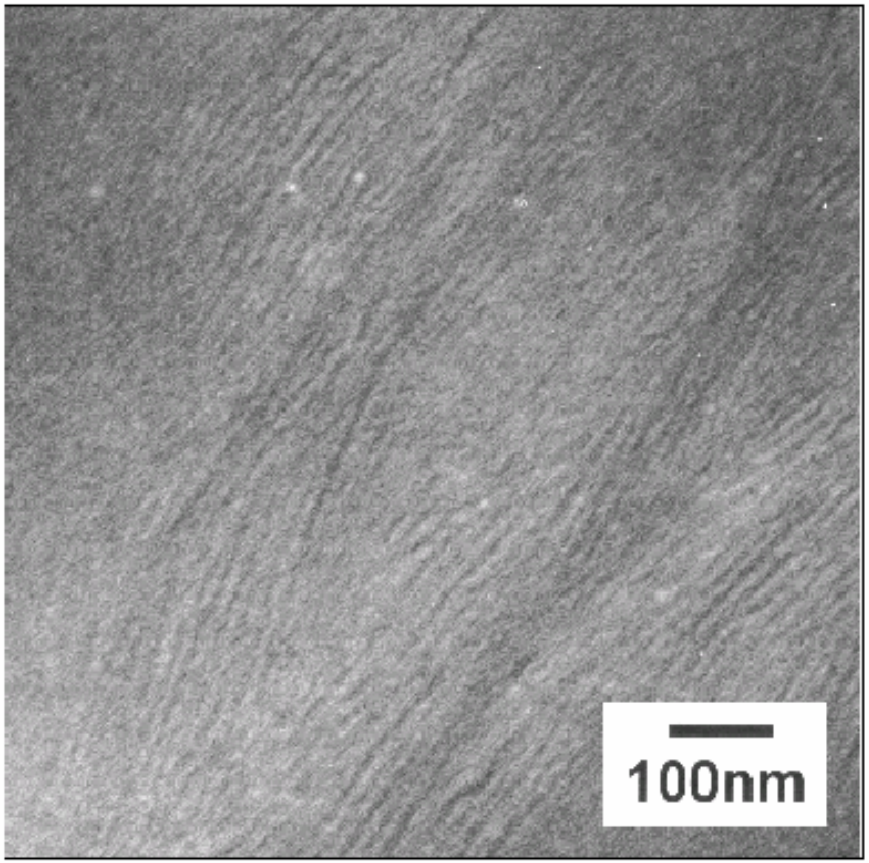
Coughlin Model Continued (building from the ground up)

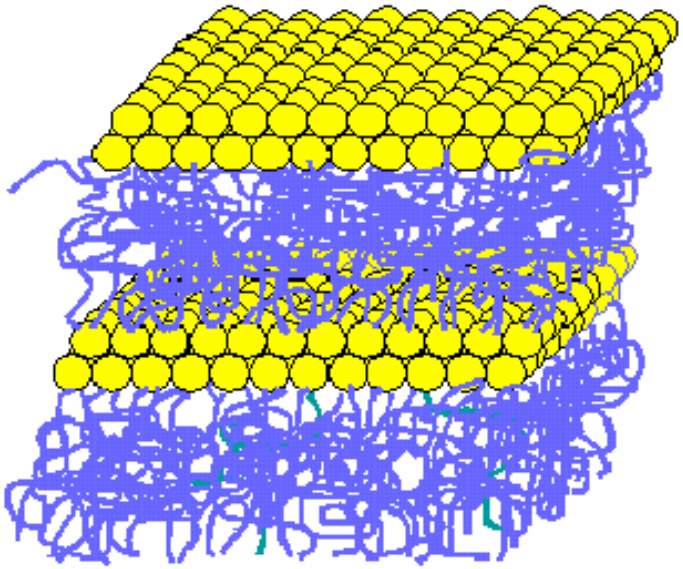


1. As a solid, POSS crystallizes



Nanoengineering with POSS



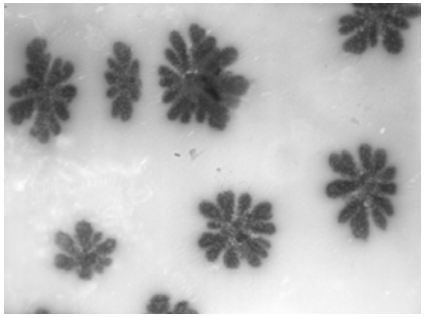


Bryan Coughlin-UMass

PBD-POSS4 (43wt%POSS)

Dimensionality Control (Crystallite/Aggregate Size)

2000 SAB



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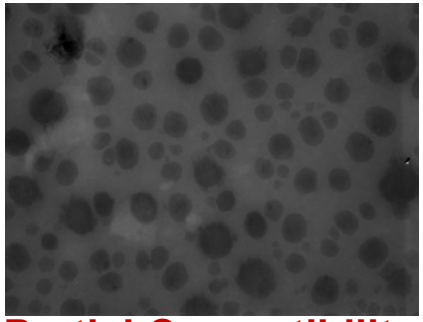
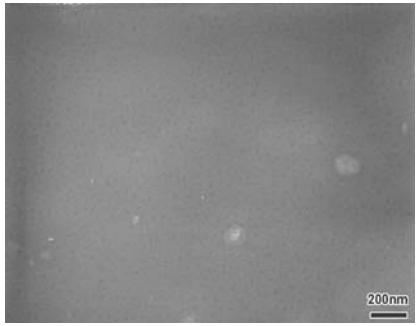


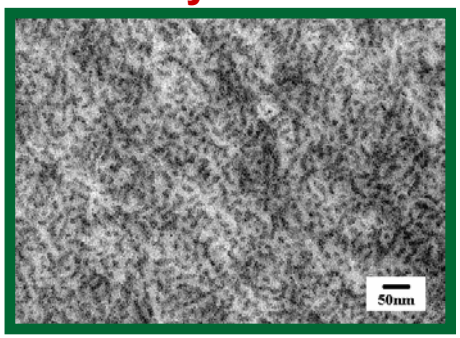
Partial Compatibility



Complete Nanodispersion

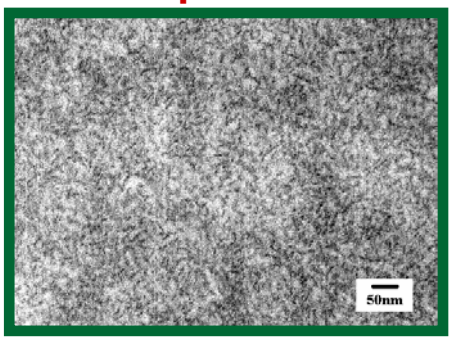
2002 SAB →

50% CyPOSS/PN



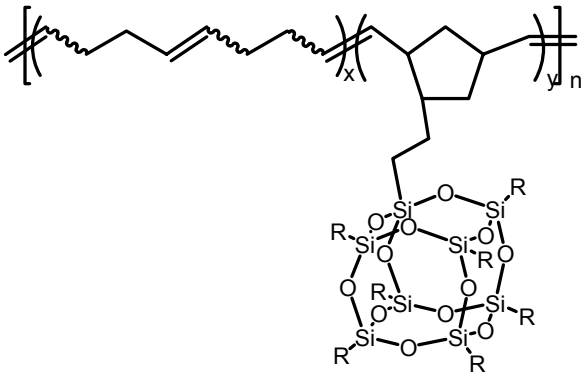
12 nm coarse cylinders
(2x ↑T_g over CpPOSS)

50% CpPOSS/PN

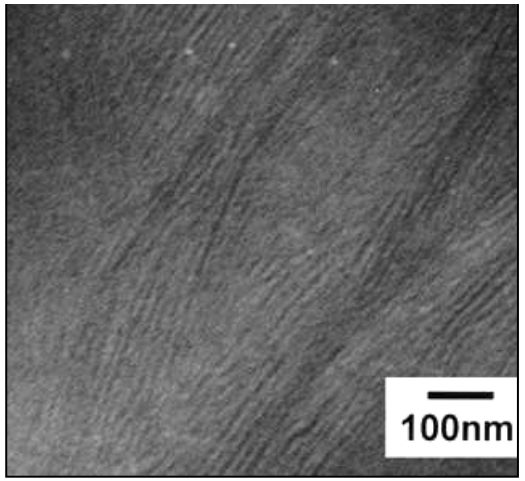


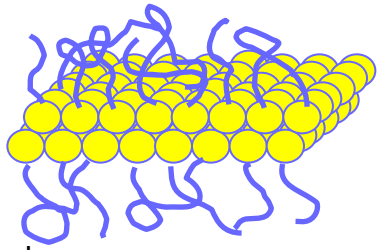
6 nm fine cylinders

2004 SAB →

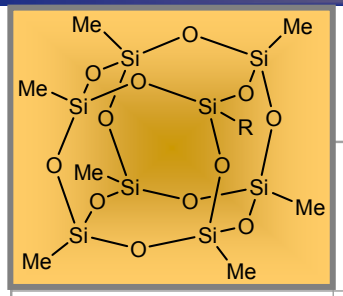


PBD-POSS (43wt%POSS)





Prof. Andre Lee i-PP/POSS Blends

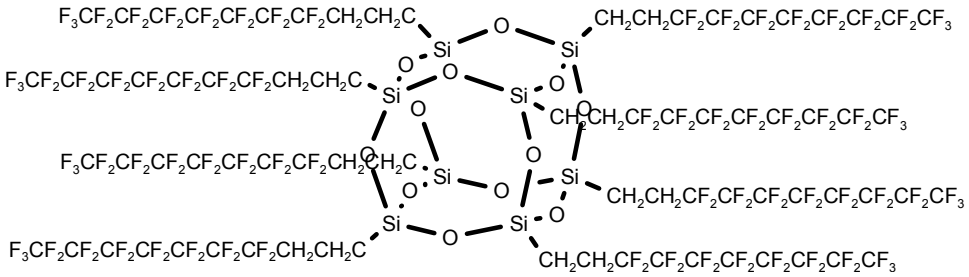


	Dow data	Neat *i*-PP (processed)	*i*-PP blended 2 wt% $Methyl_8T_8$	*i*-PP blended 5 wt% $Methyl_8T_8$	*i*-PP blended 10 wt% $Methyl_8T_8$
Tensile Strength @ Yield; ASTM D638	5000 psi (34.5 MPa)	4800 psi (33.0 MPa)	5000 psi (34.5 MPa)	5100 psi (35.1 MPa)	5200 psi (35.8 MPa)
Flexural Modulus (0.05 in/min); ASTM D790A	240,000 psi (1.655 GPa)	235,000 psi (1.620 GPa)	251,000 psi (1.730 GPa)	255,000 psi (1.757 GPa)	262,000 psi (1.80 GPa)
HDT @ 66 psi, as injected; ASTM D648	210 °F (99 °C)	210 °F (99 °C)	221 °F (105 °C)	239 °F (115 °C)	255 °F (124 °C)
Impact Izod @25C ASTM D256A	0.5 ft-lb/in	0.55 ft-lb/in	0.55 ft-lb/in	0.62 ft-lb/in	0.75 ft-lb/in

- **The above data (other than Dow's data) is an average of at least 10 samples for each test with acceptable S.D. of 5% or better.**

Seals and Gaskets

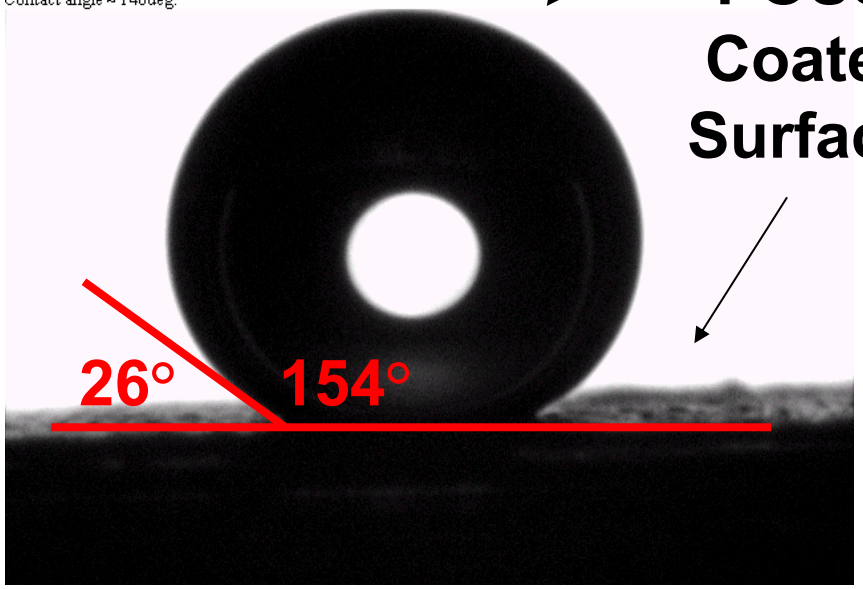
POSS Fluoromonomers and blends



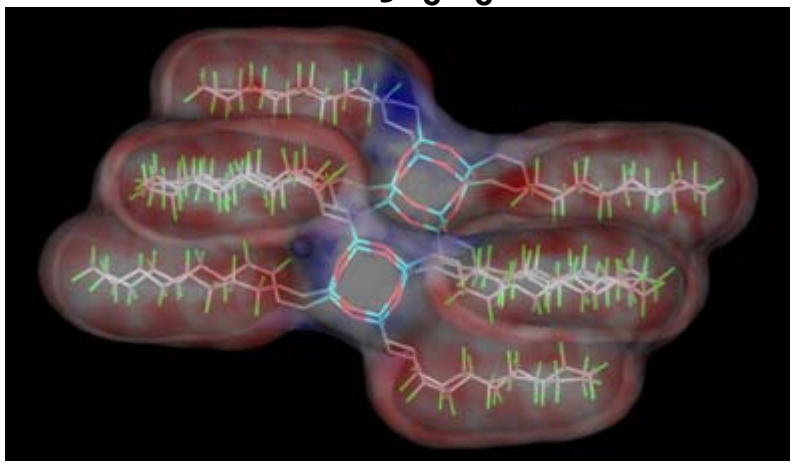
Drop of H_2O

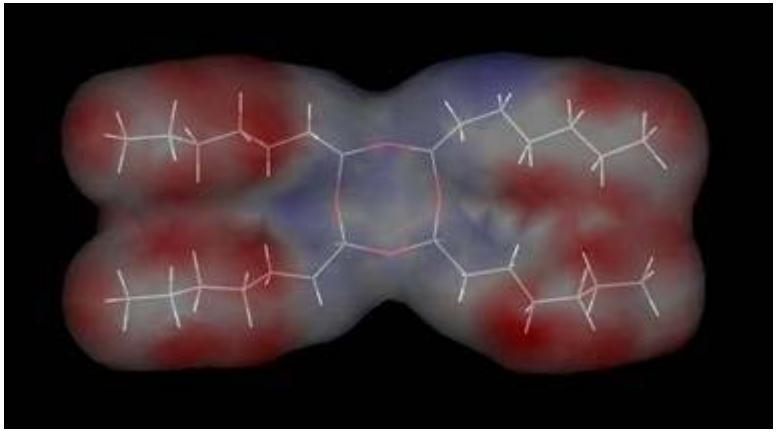
12/12/02
a drop of water on a flourinated mica surface in air and at room temperature.
Contact angle ~ 140deg.

POSS Coated Surface



Fluorodecyl$_8$T$_8$ = 154°



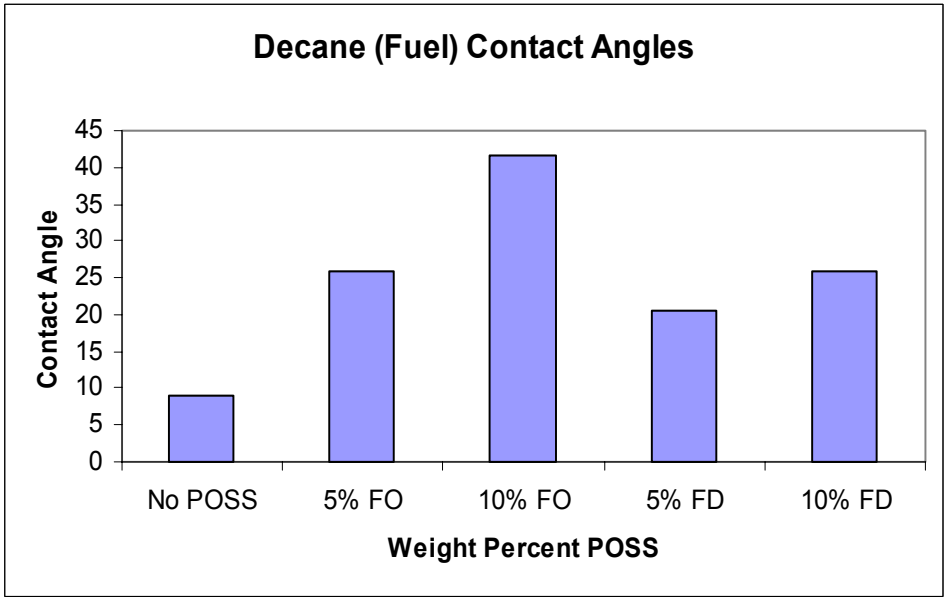


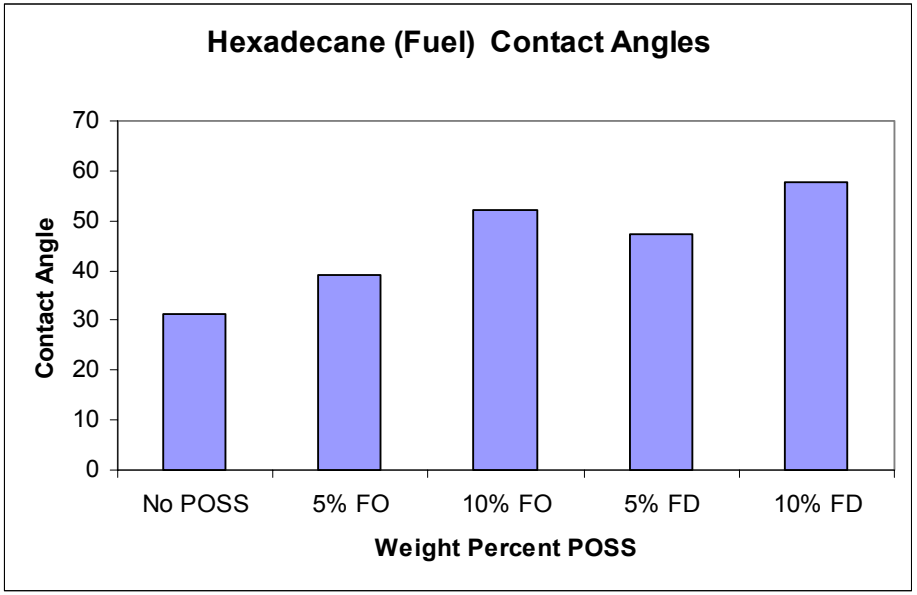
Fluorohexyl$_8$T$_8$ = 117°

Teflon = 112 °

Oleophobicity Improvement

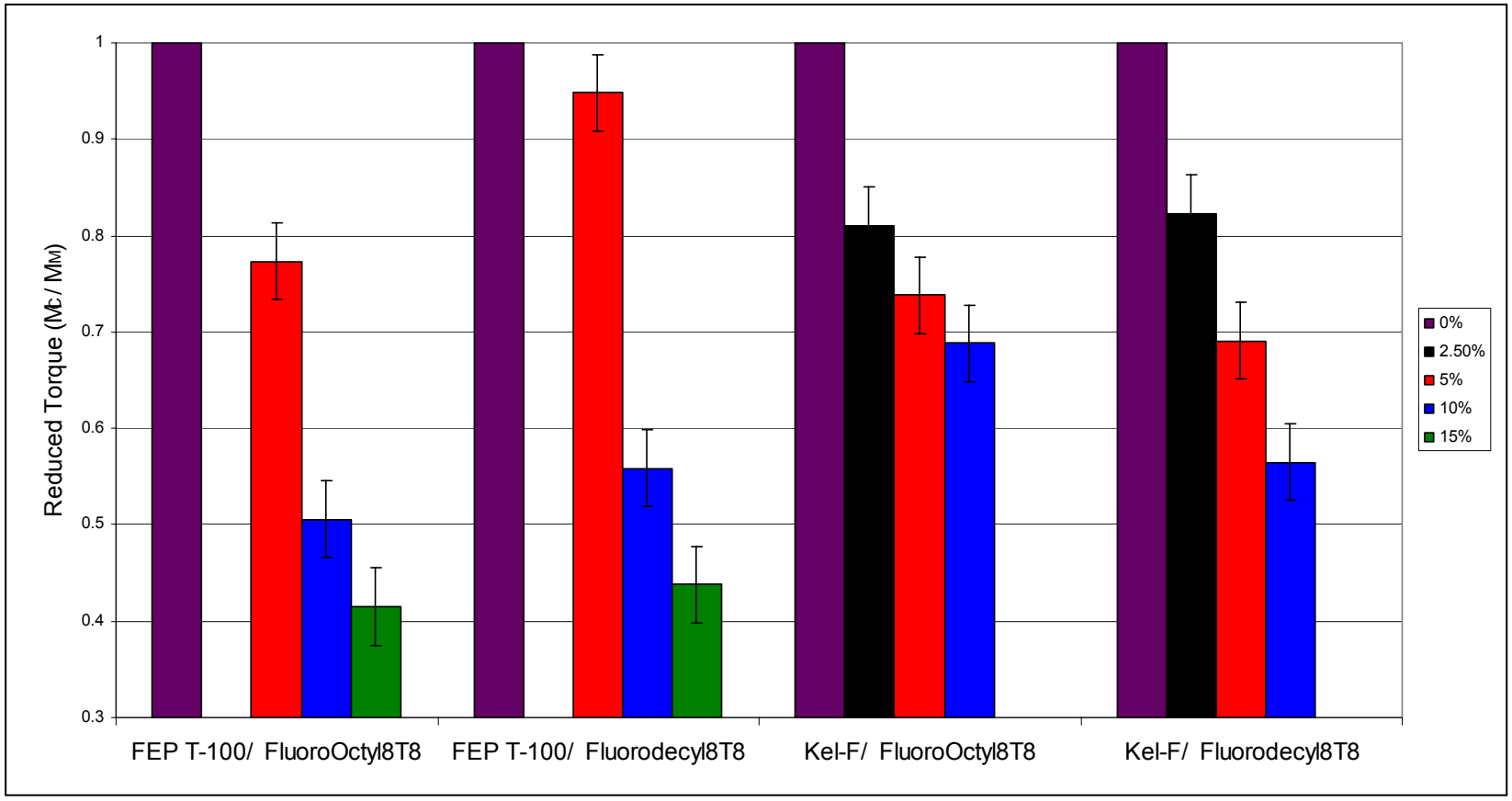
Kel-F (PCTFE) & POSS Blends





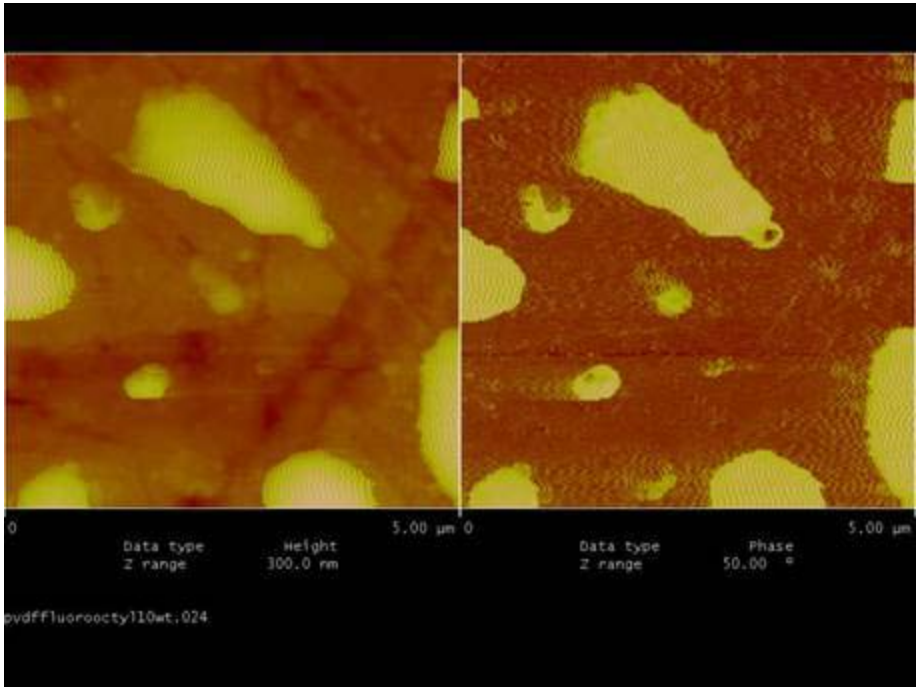
- 10 wt% FluoroPOSS in Kel-F increases the contact angle (decane: 9° → 42°, hexadecane: 31° → 58°.

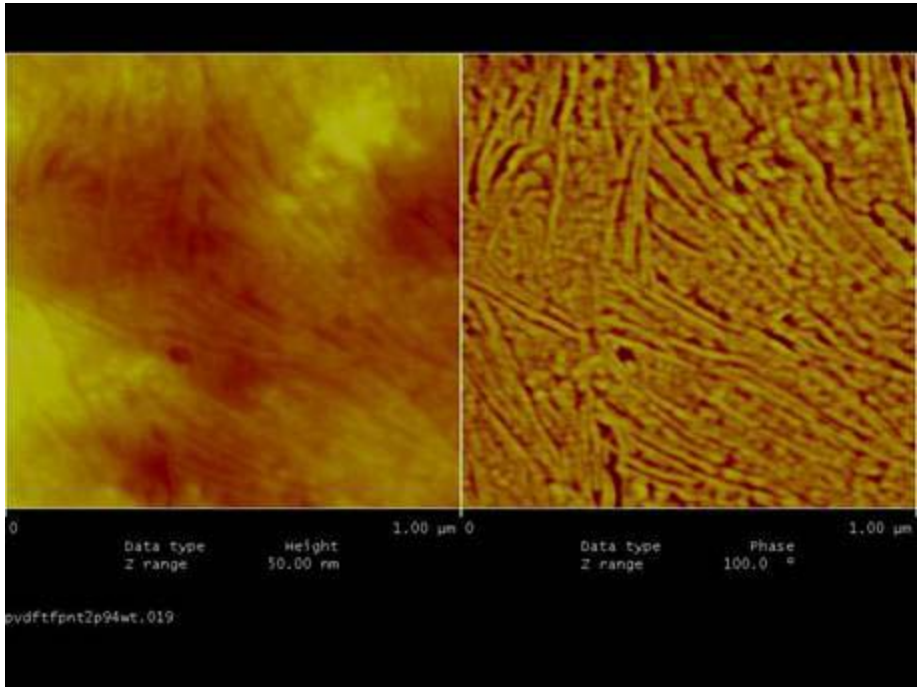
Fluoropolymer Processing Aid



- FluoroPOSS acts as a processing aid during the blending into both FEP and Kel-F without affecting the mechanical properties.

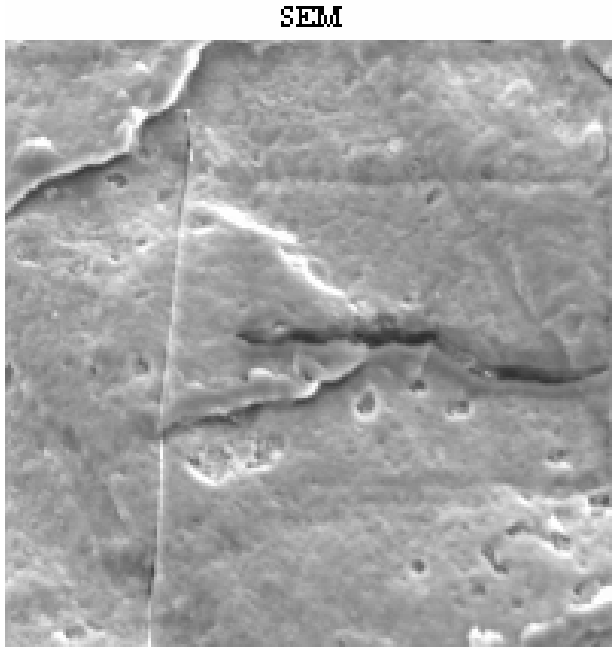
PVdF/FluoroPOSS AFMs



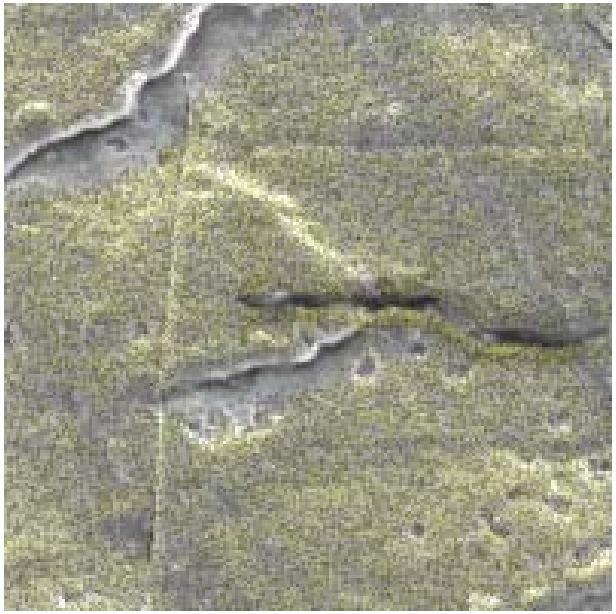


- **Fluorooctyl POSS is largely incompatible with PVdF, probably due to its large fluorine content.**
- **Fluoropropyl POSS, on the other hand, is highly compatible with PVdF. Fluoropropyl POSS has a similar F/H ratio to PVdF.**

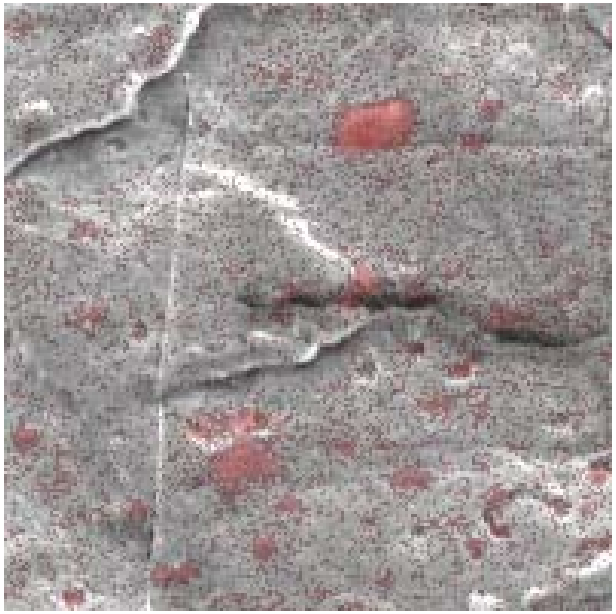
PVdF/FluoropropylnTn SEMs



SEM Image



Carbon Map

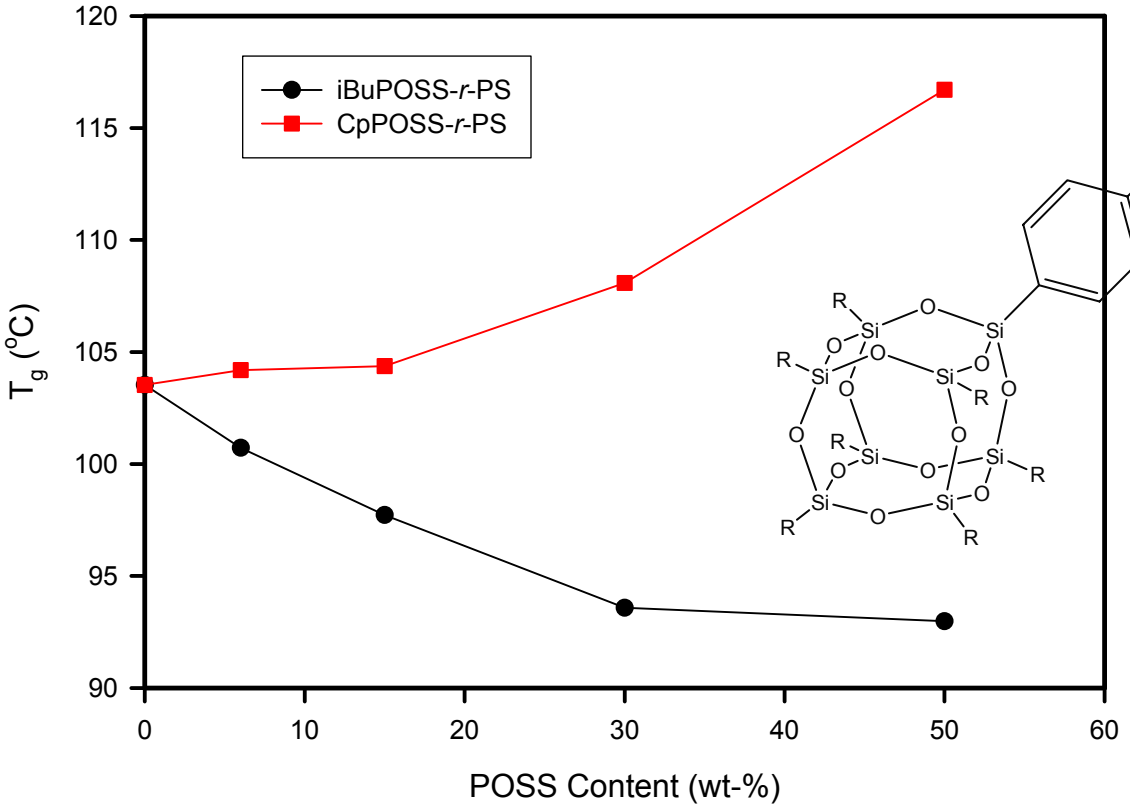


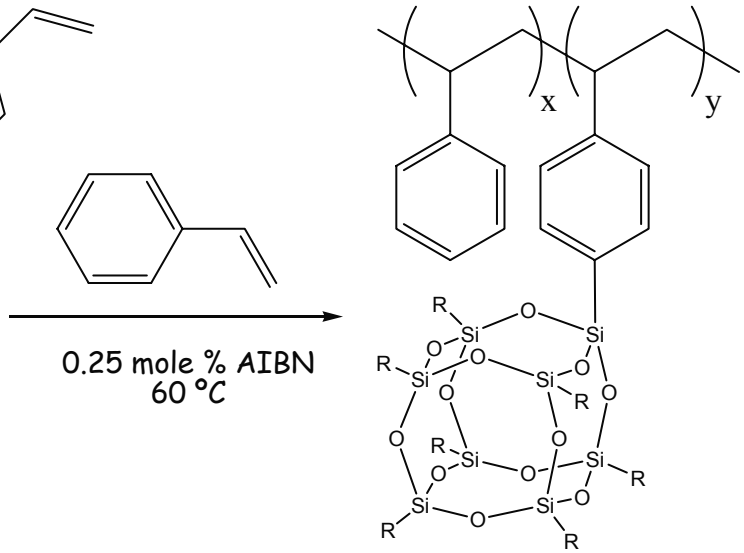
Silicon Map

- SEM Image taken on cross-section of ¼ inch thick sample bar.
- Good dispersion is observed in silicon map.

Glassy Polymer
POSS-Polystyrene

- In 2Q03 developed high molecular weight POSS-Polystyrene (R=Cy, Cp, i-Bu) resulted in:
  - Chain entanglement criteria, Good mechanical properties, Processability



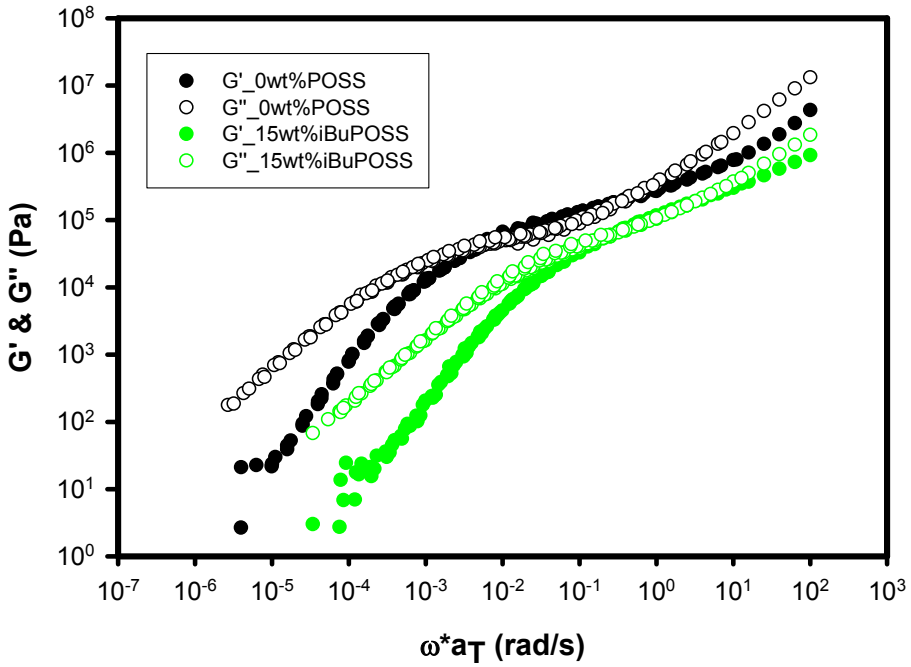


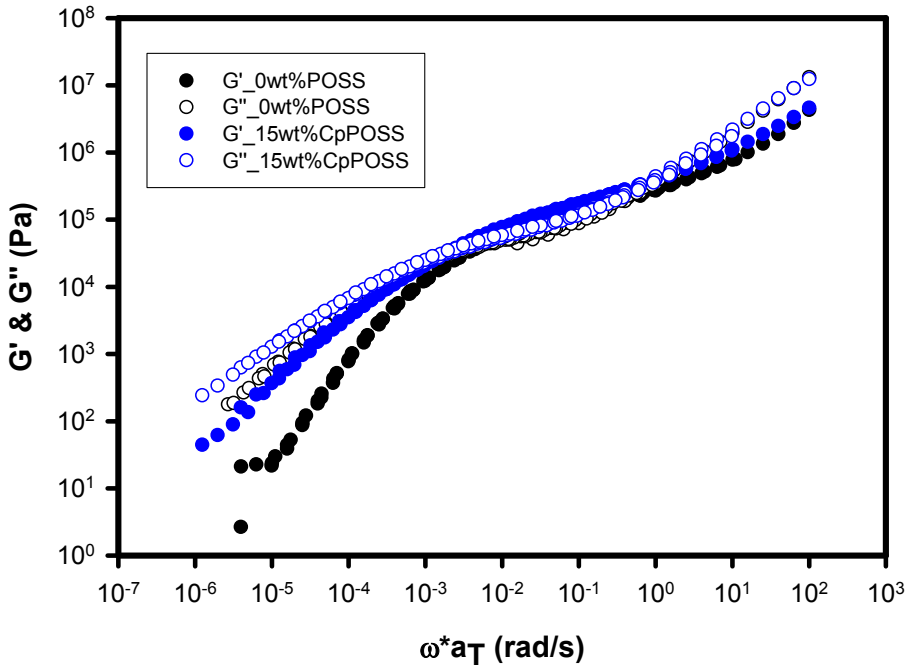
Glassy Polymer
POSS-Polystyrene

University of Connecticut

- In 2Q03 developed high molecular weight POSS-Polystyrene (R=Cy, Cp, i-Bu) resulted in:
  - Chain entanglement criteria, Good mechanical properties, Processability

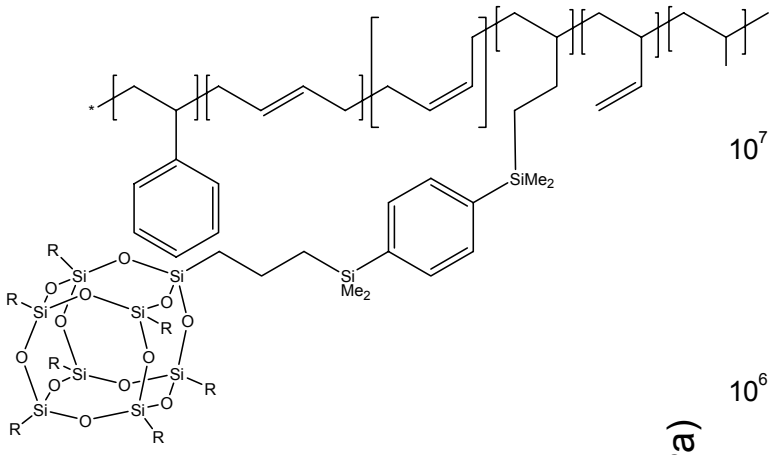
Reference Temperature = 120°C, 15% POSS



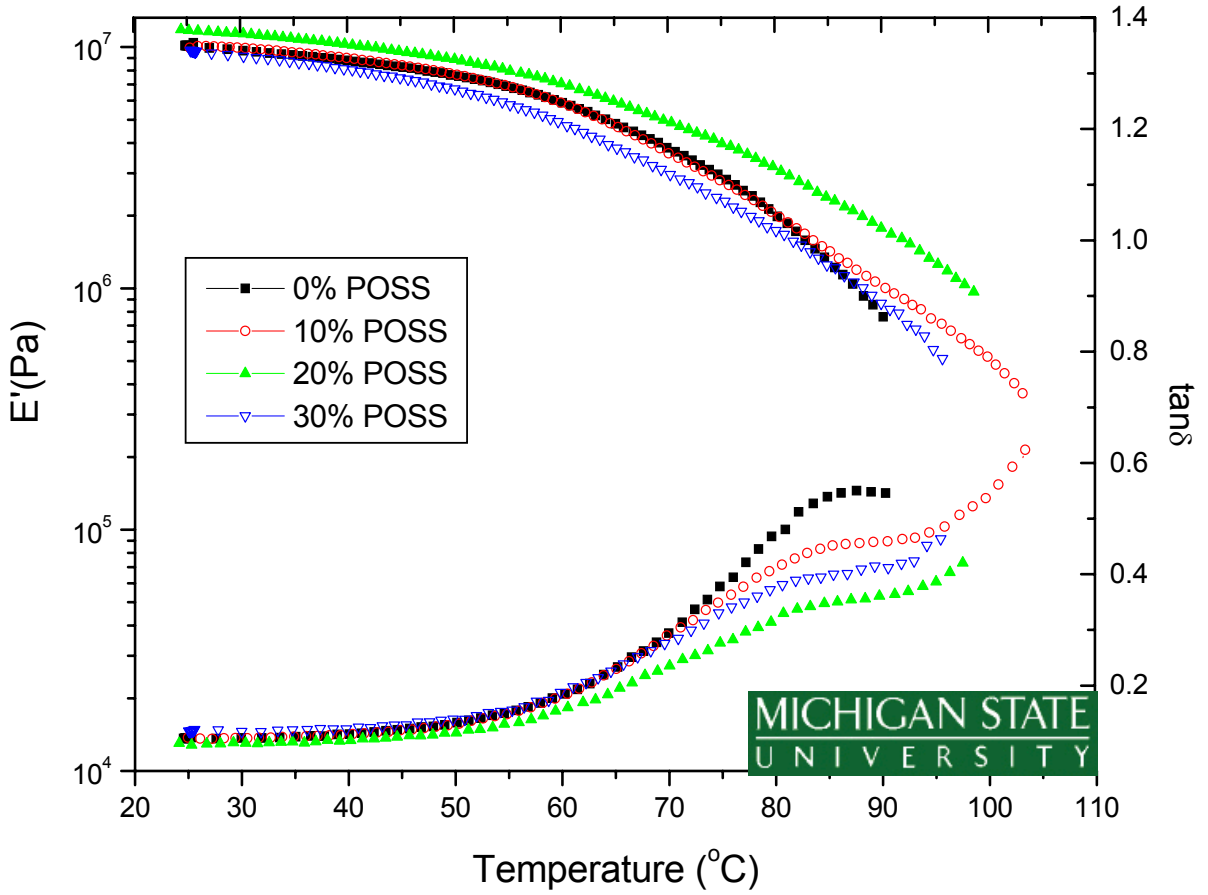


POSS-Kraton Copolymer

POSS sytrene-budadiene-styrene (SBS) copolymer



- **20 wt% POSS sample had the best retaining modulus.**
- **POSS reinforces both styrene & butadiene segments.**



- **POSS-SBS copolymers have much better high temperature performance.**

Nanostructured™ POSS Chemicals Physical Form of Products

Hybrid Plastics™

Crystalline Solids
Wide melting range 24°C to 400°C+

Waxes

Liquids & Oils
Wide viscosity range 40cSt. to 400cSt

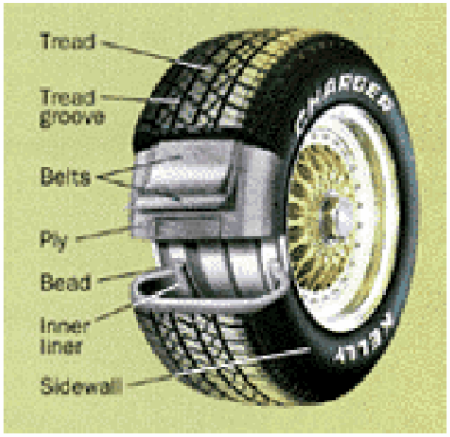
>120 POSS Monomers, Polymers and Feedstocks Available

Dave Scheraldi: POSS PET

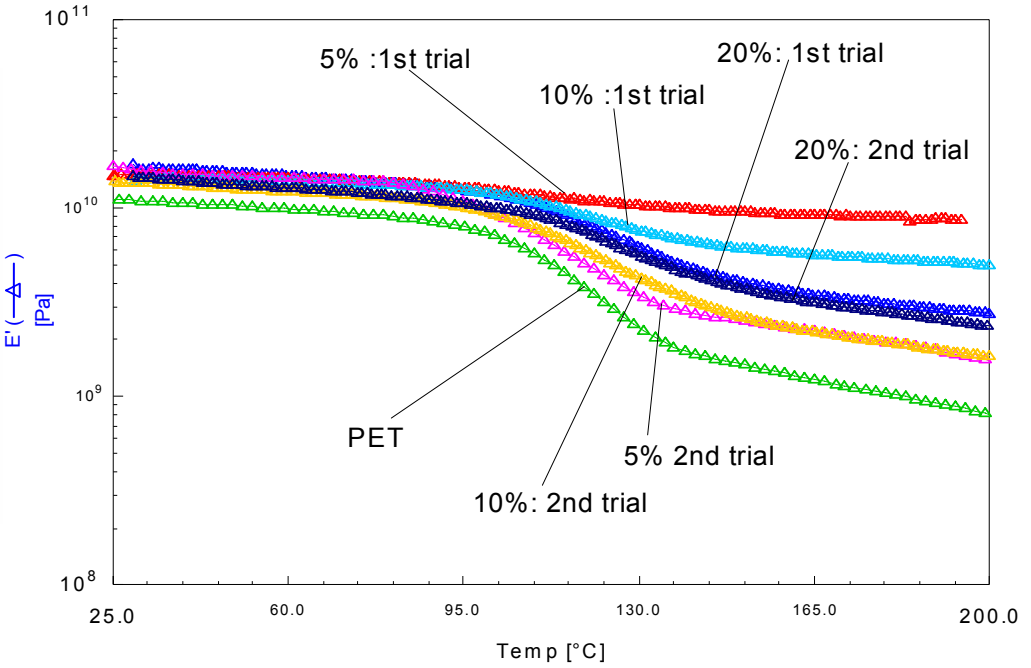
Tires are typically Reinforced with PET Fabrics

PET Tg
polymer 78° C
HMLS yarn ~ 110° C

Internal Tire Temperature
~ 120° C



TrisilanolisooctylPOSS PET Blend



Scheraldi (Case Western) and KOSA investigating processing parameters for POSS blended with PET tire cord

Masanori Ikeda: Flame resistant POSS PPE

Asahi-KASEI Corporation: Hybrid Plastics Asian Distributor

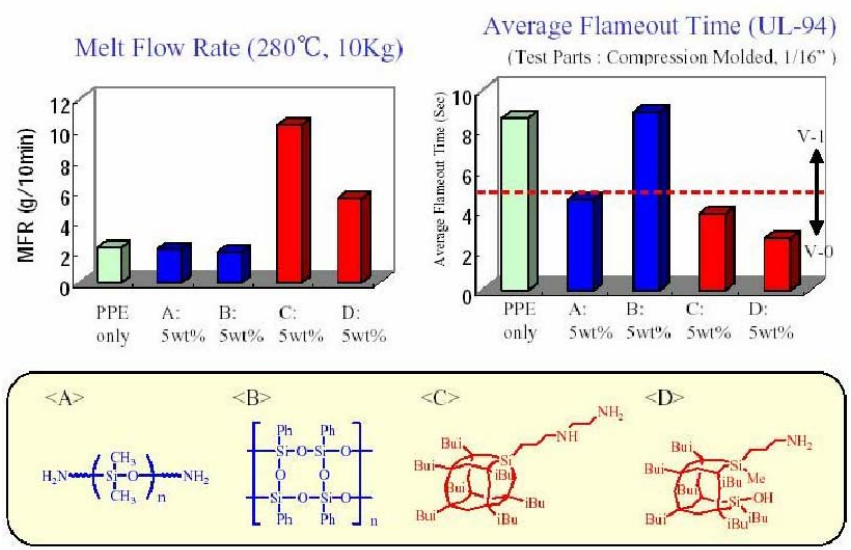


Figure 8. Effects of Additives on MFR and Anti-Flammability

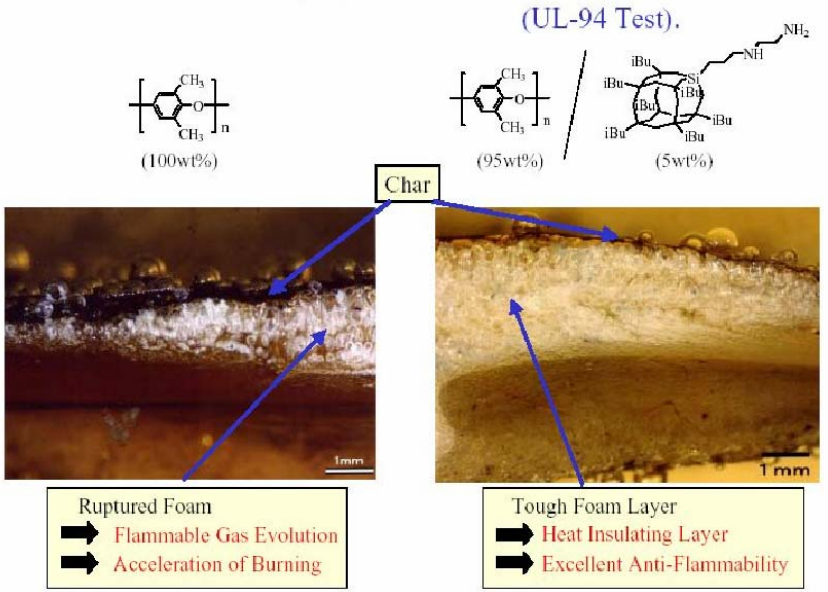
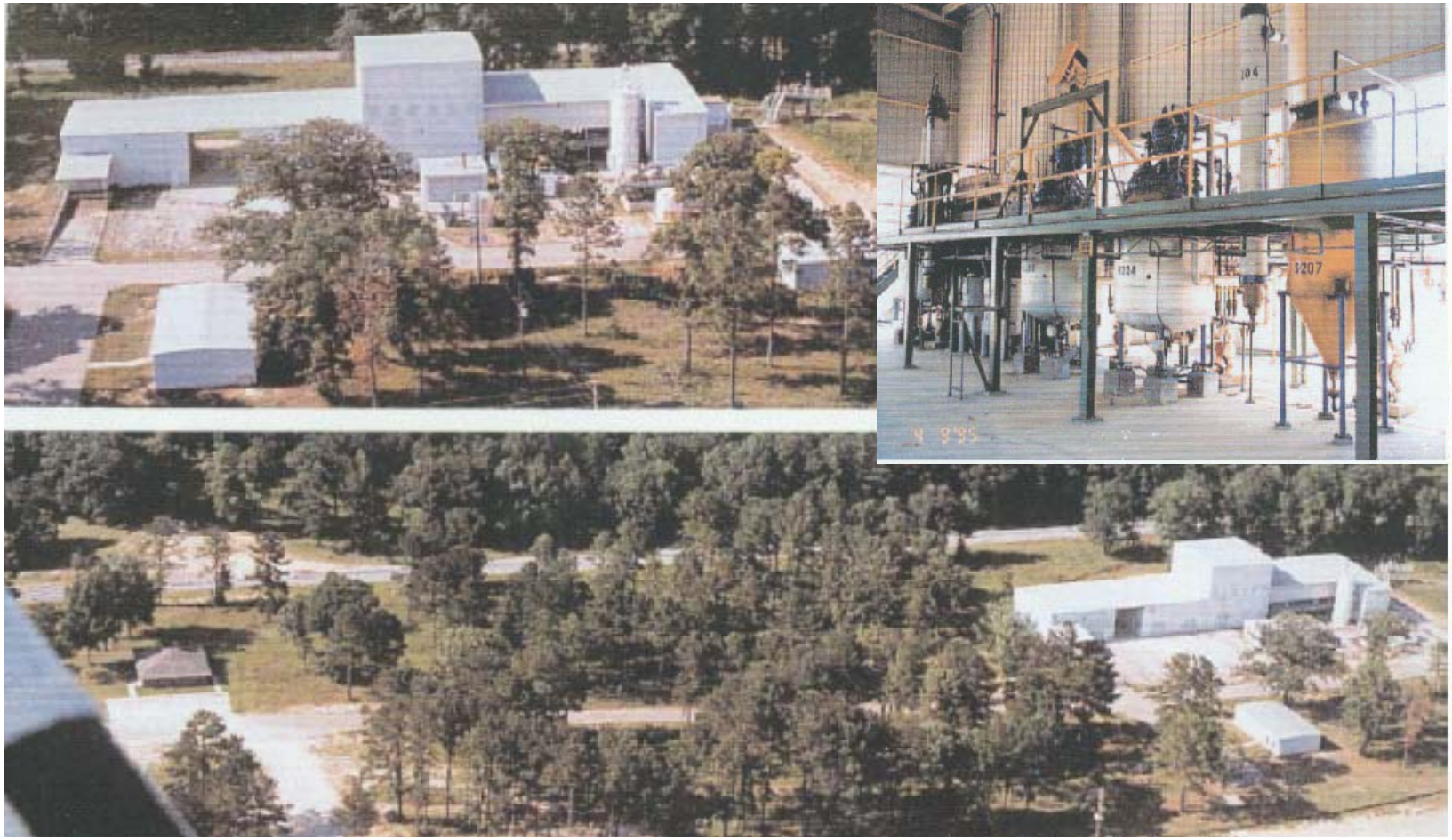


Figure 10. Cross Section Photograph of Burned Test Piece

Isobutyl POSS cage in PPE gives:
- **superior flame retardance**
- **imparts superb processability**
- **excellent HDT is maintained**

File name

Hybrid Plastics
Tech Transfer Partner (The Nanotech Part)



Southern Mississippi – Corporate Headquarters and Production

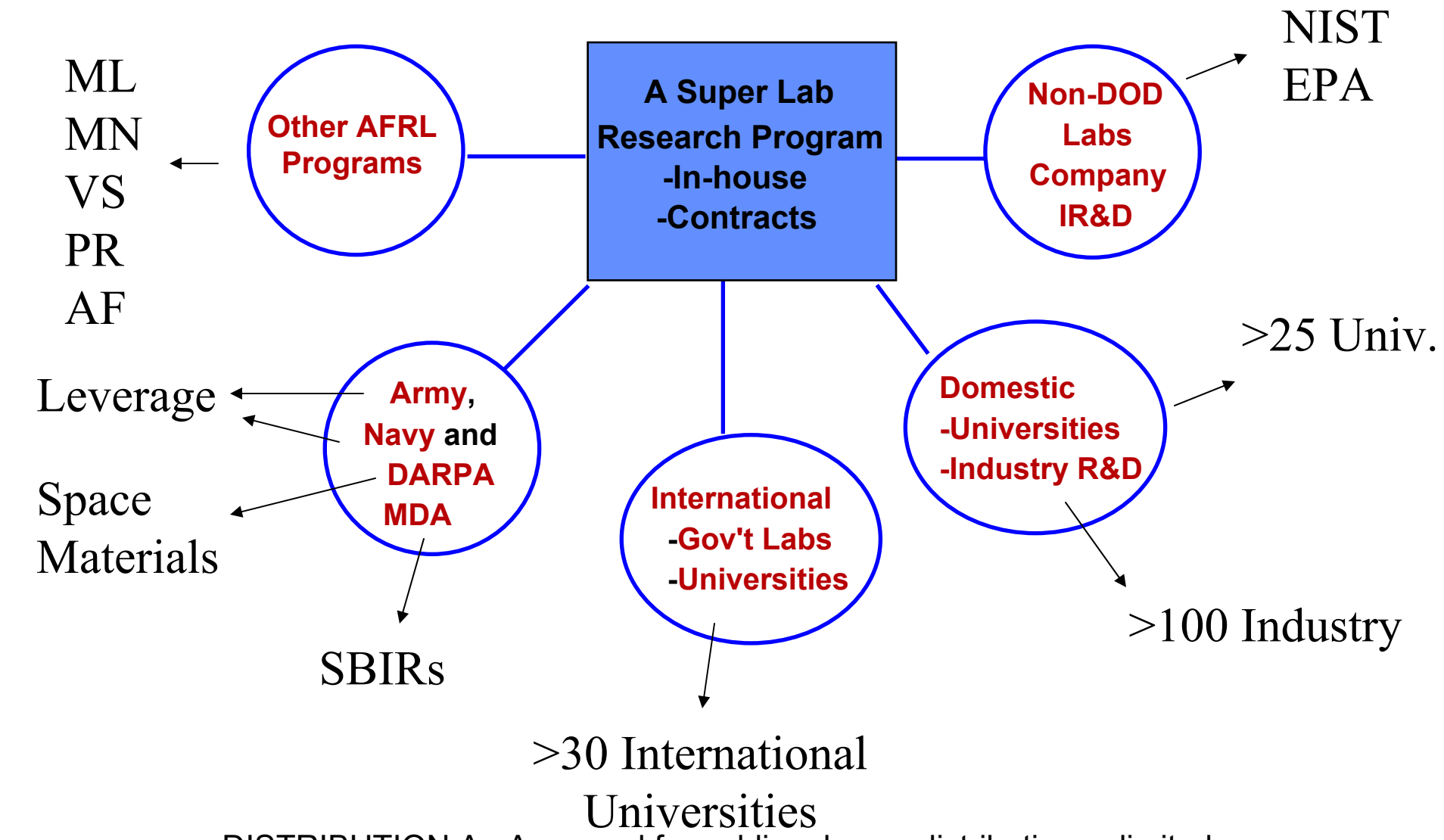
Southern California – Laboratory and Chemistry Research

USM “Southern Miss” Lab – Technical Support & Polymer Formulation

Hybrid Plastics: 4’x8’ Panel

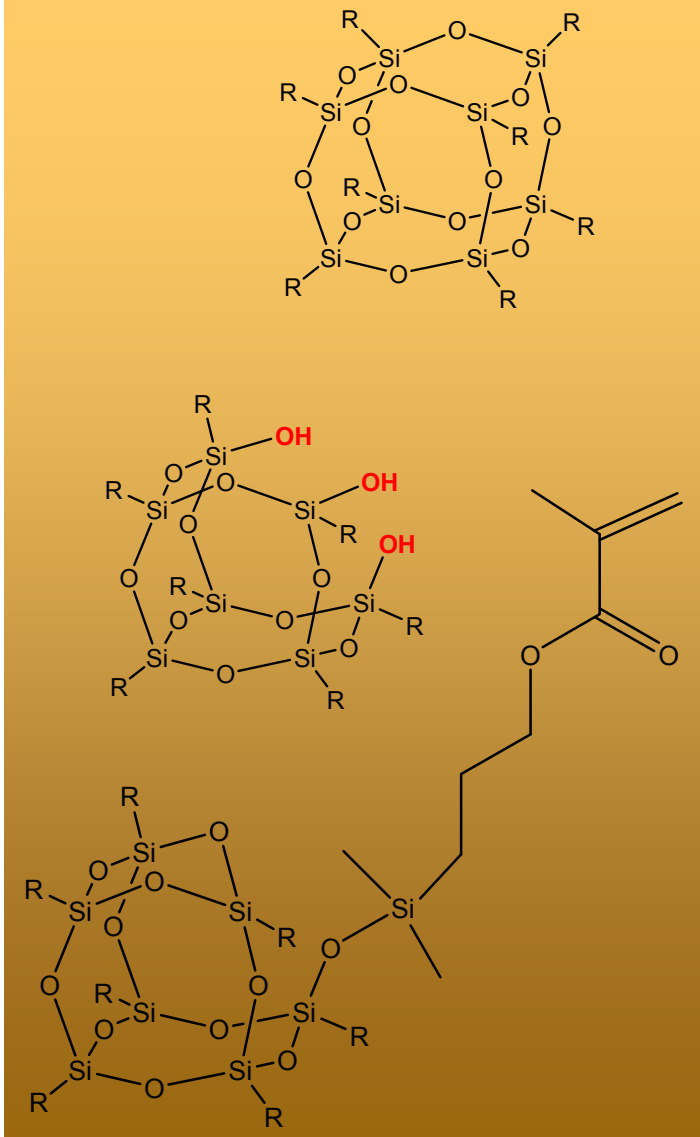
VARTM of 4’x8’ panel

A Super Lab Created from the Ground Up (AFRL Edwards)



POSS: Where Are We Now (2004)
1996 data in red

- **Cost: $20-$5000/lb ($5000-$10,000/lb)**
- **Volume: Multi-ton (~20lb/yr)**
- **Production time: min 1 hour (11 days), max 14 days (6 months)**
- **Versatility: >120 POSS (36 POSS) monomers, feedstocks, polymers**
- **Many successful POSS blends**
- **Commercialized by Hybrid Plastics www.hybridplastics.com**



Why Use POSS?

- **Multifunctionality – including no negative effects on processing (or can even get improvements)**
- **Properties previously not attainable (extended temp range, flame retardancy)**
- **Turnkey Utility**
- **The ultimate control of molecular architect**